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**Patentanmeldung Nr.    Patent application No.    Demande de brevet n°**

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Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

**R C van Dijk**



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(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.  
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Antifouling coating composition and its use on man made structures in a fresh water environment

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**ANTIFOULING COATING COMPOSITION AND ITS USE ON MAN MADE  
STRUCTURES IN A FRESH WATER ENVIRONMENT**

This invention relates to an antifouling coating composition which is in particular  
5 suited to be used as coating on man-made structures immersed in a low-salinity  
aquatic environment.

Man-made structures such as boat hulls, buoys, drilling platforms, oil production  
rigs, and pipes which are immersed in water are prone to fouling by aquatic  
10 organisms such as green and brown algae, barnacles, mussels, and the like.  
Such structures are commonly of metal, but may also comprise other structural  
materials such as concrete. This fouling is a nuisance on boat hulls, because it  
increases frictional resistance during movement through the water, the  
consequence being reduced speeds and increased fuel costs. It is a nuisance  
15 on static structures such as the legs of drilling platforms and oil production rigs,  
firstly because the resistance of thick layers of fouling to waves and currents  
can cause unpredictable and potentially dangerous stresses in the structure,  
and, secondly, because fouling makes it difficult to inspect the structure for  
defects such as stress cracking and corrosion. It is a nuisance in pipes such as  
20 cooling water intakes and outlets, because the effective cross-sectional area is  
reduced by fouling, with the consequence that flow rates are reduced.

It is common practice in the marine construction industry for ships and other  
man-made objects to be fabricated on land or in a floating dry-dock and then  
25 launched or floated out after completion of the main structure. Fabrication of  
the ship or other man-made object may then be completed and the structure  
fitted-out while it is immersed in an aquatic environment. In many countries, for  
example in Europe, such as Romania, or in China, ships and other man-made  
objects are often launched into a low salinity or fresh water aquatic environment  
30 such as the Baltic Sea, or a river or river estuary. Many such structures will  
then subsequently encounter an ocean water or other aquatic environment with

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a higher salinity during its normal operation. Normally, protective coatings will be applied to the structure prior to immersion. An antifouling paint will be applied as a top-coat on immersed areas of the structure to inhibit the settlement and growth of aquatic organisms such as barnacles and algae, generally by the release of a biocide for the aquatic organisms. Such antifouling paints should additionally have appropriate physical and mechanical properties to withstand extended immersion in fresh water, ocean water and intermediate aquatic environments and preferably they should also be able to withstand changes in the salinity of the aquatic environment, for example when a ship regularly travels between a river or river estuary and the ocean.

Traditionally, antifouling paints have comprised a relatively inert binder with a biocidal pigment that is leached from the paint. Among the binders which have been used are vinyl resins and rosin or rosin derivatives. Vinyl resins are water-insoluble and paints based on them use a high pigment concentration so as to have contact between the pigment particles to ensure leaching. Rosin is a hard brittle resin that is very slightly soluble in water. Rosin-based antifouling paints have been referred to as soluble matrix or eroding paints. The biocidal pigment is very gradually leached out of the matrix of rosin binder in use, leaving a skeletal matrix of rosin, which becomes washed off the hull surface to allow leaching of the biocidal pigment from deep within the paint film.

Many successful antifouling paints in recent years have been "self-polishing copolymer" paints based on a polymeric binder to which biocidal tri-organotin moieties are chemically bound and from which the biocidal moieties are gradually hydrolysed in an aquatic environment. In such binder systems, the side groups of a linear polymer unit are split off in a first step by reaction in the aqueous medium, the polymer framework that remains becoming water-soluble or water-dispersible as a result. In a second step, the water-soluble or water-dispersible framework at the surface of the paint layer on the ship is washed

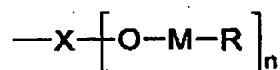
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out or eroded. Such paint systems are described for example in GB-A-1 457 590.

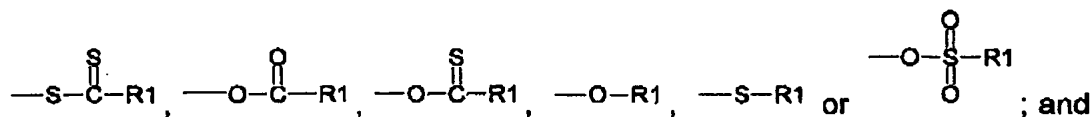
As the use of tri-organotin has been prohibited world-wide, there is a need for alternative antifouling substances that can be used in antifouling compositions. Self-polishing copolymer paints, which release non-biocidal moieties, are described in EP-A-69 559, EP-A-529 693, WO-A-91/14743, WO-A-91/09915, GB-A-231 070, and JP-A-9-286933.

Very promising self-polishing copolymer paints which release non-biocidal moieties are disclosed for example in EP-A-204 456 and EP-A-779 304. The binder used in the paints comprises an acrylic backbone bearing at least one terminal group of the formula:



wherein X represents  $-\overset{\text{O}}{\parallel}{C}-$ ,  $-\overset{\text{S}}{\parallel}{C}-$ ,  $-\overset{\text{O}}{\parallel}{P}-$  or  $-\overset{\text{O}}{\parallel}{P}-$

M is a metal selected from zinc, copper and tellurium; n is an integer of 1 to 2; R represents an organic residue selected from



R<sub>1</sub> is a monovalent organic residue.

Usually the binder is mixed with a biocide for aquatic organisms.

Commercially successful antifouling paints of this type most commonly comprise a binder in which X is  $-\overset{\text{O}}{\parallel}{C}-$ , M is copper, R represents  $-O-\overset{\text{O}}{\parallel}{C}-R_1$ , and the binder is mixed with cuprous oxide and a biocidal zinc

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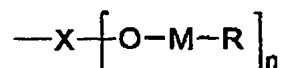
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compound such as zinc pyrithione. Such paints generally have excellent and durable physical and mechanical properties when immersed in a salt water or brackish aquatic environment but it was found that they may exhibit excessive softening, cracking, blistering or delamination upon exposure in a fresh water or low salinity aquatic environment.

More recently, antifouling paints have been developed where the binder comprises a rosin material and an auxiliary film-forming resin, the auxiliary film-forming resin comprising an acid-functional film forming polymer whose acid groups are blocked by groups capable of hydrolyzing, dissociating or exchanging with seawater species to leave a polymer soluble in seawater, and optionally a portion of a non-hydrolyzing water-insoluble film-forming polymer. Such paints are described in WO 02/02698. These and other rosin based paints generally show less durable antifouling performance than rosin-free self polishing antifouling paints and also generally have poorer physical and mechanical properties upon immersion in a fresh water or low salinity aquatic environment than in an ocean water or high salinity aquatic environment.

Surprisingly it was found that very good anti fouling and protective properties for a man-made structure immersed in a fresh water or low salinity aquatic environment can be achieved when the immersed portion of the structure is coated with a paint that is substantially free of any biocidal zinc moieties and substantially free of rosin, comprising a copper-based biocide for aquatic organisms having a metallic copper content below 2 % by weight, based on the total weight of the copper-based biocide and a film-forming resin comprising

- 20-100% by weight of a film-forming polymer (A) having an acrylic backbone bearing at least one terminal group of the formula:

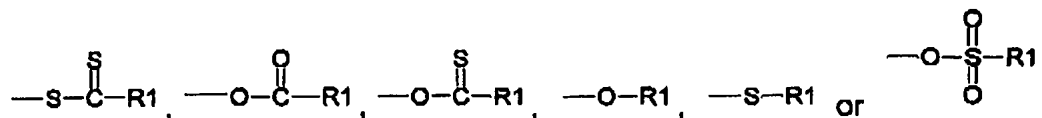


wherein X represents  $-\overset{\text{O}}{\parallel}{C}-$ ,  $-\overset{\text{S}}{\parallel}{C}-$ ,  $-\overset{\text{O}}{\parallel}{P}-$  or  $-\overset{\text{O}}{\parallel}{P}-$

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M is a copper or tellurium; x is an integer of 1 to 2; R represents an organic residue selected from



and R1 is a monovalent organic residue, and

- 6 - 80-0% by weight of a non-hydrolyzing water-insoluble film-forming polymer (B).

Preferably, the film-forming polymer (A) is an acrylic polymer in which X represents

- 10  $\text{—C(=O)—}$ , M is copper and R represents  $\text{—O—C(=O)—R1}$ . The parent acrylic polymer having a -COOH group in place of -X-[O-M-R]<sub>x</sub> preferably has an acid value of 25-350 mg KOH/g. Most preferably the hydrolysable polymer has a copper content of 0.3-20% by weight and R<sup>1</sup> is the residue of a high boiling organic monobasic acid. Such hydrolysable polymers can be prepared by the
- 15 processes of EP-A-204456 and EP-A-342276. The copper-containing film-forming polymer (A) is preferably a copolymer comprising an acrylic or methacrylic ester whose alcohol residue includes a bulky hydrocarbon radical or a soft segment, for example a branched alkyl ester having 4 or more carbon atoms or a cycloalkyl ester having 6 or more atoms, a polyalkylene glycol
- 20 monoacrylate or monomethacrylate optionally having a terminal alkyl ether group or an adduct of 2-hydroxyethyl acrylate or methacrylate with caprolactone, as described in EP-A-779304.

- The film-forming polymer (A) can be a so-called high solids resin. By using such
- 25 resin, a coating composition can be obtained with a volatile organic compound (VOC) content of not more than 400 g/L, preferably of less than 350 g/L.

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The film-forming polymer (A) can be prepared as follows:

- i) polymerization of an unsaturated organic acid monomer and an additional unsaturated monomer and either reacting the resulting acrylic resin with a metal compound and a monobasic acid or reacting said acrylic resin with a metal salt of a monobasic acid or
  - ii) reacting an unsaturated organic acid monomer with a metal compound and a monobasic acid or reacting an unsaturated organic acid monomer with a metal salt of a monobasic acid and polymerizing the resulting metal-containing unsaturated monomer with another unsaturated monomer.
- In view of the higher yield method i) is preferred.

The unsaturated organic acid monomer mentioned above can be selected from the group of unsaturated compounds having at least one carboxyl group, for example unsaturated monobasic acids such as (meth) acrylic acid; unsaturated dibasic acids and monoalkyl esters thereof, such as maleic acid inclusive of its monoalkyl esters and itaconic acid inclusive of its monoalkyl esters; unsaturated monobasic acid hydroxyalkyl ester-dibasic acid adducts, such as 2-hydroxyethyl (meth)acrylate-maleic acid adduct, 2-hydroxyethyl (meth)acrylate-phthalic acid adduct, and 2-hydroxyethyl (meth)acrylate-succinic acid adduct. In this specification, the term (meth)acrylic acid is used to mean whichever of methacrylic acid and acrylic acid.

The additional unsaturated monomer can be selected from various esters of (meth)acrylic acid, e.g. alkyl (meth)acrylates, the ester moieties of which contain 1 to 20 carbon atoms, such as methyl (meth)acrylate, ethyl (meth)acrylate, i-propyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate and stearyl (meth)acrylate; hydroxy-containing alkyl (meth)acrylates, the ester moieties of which contain 1 - 20 carbon atoms, such as 2-hydroxypropyl (meth)acrylate and 2-hydroxyethyl (meth)acrylate; cyclic



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hydrocarbon esters of (meth)acrylic acid, such as phenyl (meth)acrylate and cyclohexyl (meth)acrylate; polyalkylene glycol esters of (meth)acrylic acid, such as polyethylene glycol mono (meth) acrylate and polyethylene glycol mono (meth) acrylate with a degree of polymerization in the range of 2 to 50; C<sub>1-3</sub> alkoxyalkyl (meth)acrylate; (meth)acrylamide; vinyl compounds such as styrene, alpha -methylstyrene, vinyl acetate, vinyl propionate, vinyl benzoate, vinyltoluene and acrylonitrile; esters of crotonic acid; and diesters of unsaturated dibasic acids, such as maleic acid diesters and itaconic acid diesters. Of the above-mentioned esters of (meth)acrylic acid, the ester moieties are preferably alkyl groups containing 1 to 8 carbon atoms, more preferably an alkyl groups containing 1 to 6 carbon atoms. The preferred specific compounds are methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate and cyclohexyl (meth)acrylate.

The above-mentioned unsaturated organic acid monomers and other unsaturated monomers may each be used alone or in a mixture of two or more species.

The film-forming polymer (A) preferably has an acid value of 25 to 350 mg KOH/g. If the acid value is below 25 mg KOH/g, the amount of metal salt to be attached to the side chain is too low for effective antifouling and self-polishing properties. If it is above 350 mg KOH/g, the hydrolysis rate will be too high so that the service life of the antifouling coating is strongly reduced. In addition, such high acid value will result in a rise of the viscosity of the film-forming polymer (A), which would make it less suited for use in low VOC coatings. An acid value in the range from 100 to 250 mg KOH/g is preferred.

The antifouling coating comprises a copper-based biocide for aquatic organisms having a metallic copper content below 2 % by weight, based on the total weight of the copper-based biocide is used. Preferably, the metallic copper

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content is below 1 percent by weight, more preferably below 0.8 percent by weight, and even more preferably below 0.7 percent by weight.

The copper-based biocide for aquatic organisms with the low metallic copper content is preferably present in an amount between 1 and 75, more preferably  
6 between 5 and 75 percent by weight, even more preferably between 25 and 70 percent by weight, based upon the total weight of the coating composition.

Examples of such copper-based biocide for aquatic organisms includes compounds, such as cuprous oxide, cuprous thiocyanate, cuprous sulphate, or copper pyrithione. These copper-based biocides can be used alone or in a  
10 mixture of two or more of these compounds.

In view of the good overall physical and antifouling properties, cuprous oxide with a low metal content is the preferred copper-based biocide for use in the antifouling coating composition according to the present invention. Since cupric oxide is often present as an impurity in cuprous oxide, the coating composition  
15 may contain an amount of cupric oxide of up to 10 percent by weight, preferably up to 6 percent by weight, more preferably up to 3 percent by weight, based on the total weight of cuprous oxide.

In a further preferred embodiment, the antifouling coating composition according to the present invention comprises a mixture of cuprous oxide having  
20 a metallic copper content below 2 % by weight and copper pyrithione.

The coating composition preferably has a pigment volume concentration of, for example, 15 to 55%.

25 In addition to the film-forming polymer (A), the anti-fouling coating compositions according to the present invention optionally comprise another film-forming polymer (B). Polymer (B) comprises one or more resins which are free of -X-[O-M-R]<sub>n</sub> terminal groups but which are reactive in water, slightly water-soluble or water-sensitive, or insoluble in water.

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In addition to the copper-based biocide for aquatic organisms having a metallic copper content below 2 % by weight, the antifouling coating compositions according to the present application optionally comprise an additional ingredient having biocidal properties for aquatic organisms

5 Further, the antifouling coating compositions may comprise one or more non-biocidal pigments, and/or additives such as one or more thickening or thixotropic agents, one or more wetting agents, plasticisers, fillers, a liquid carrier such as an organic solvent, organic non-solvent or water, etc.

10 Examples of resins that can be used in addition to the film-forming polymer (A) in the anti-fouling coating composition used in accordance with the present invention include polymers which are free of  $-X-[O-M-R]_n$  terminal groups but which are reactive in water, resins which are slightly soluble or water-sensitive in water, and resins which are insoluble in water.

15

As examples of a suitable polymer (B) that is free of  $-X-[O-M-R]_n$  terminal groups but which are reactive in water, several resins can be mentioned.

For instance, an example of a suitable polymer is an acid-functional film-forming polymer, the acid groups of which are blocked by quaternary ammonium groups or quaternary phosphonium groups. This is for instance  
20 described in WO 02/02698.

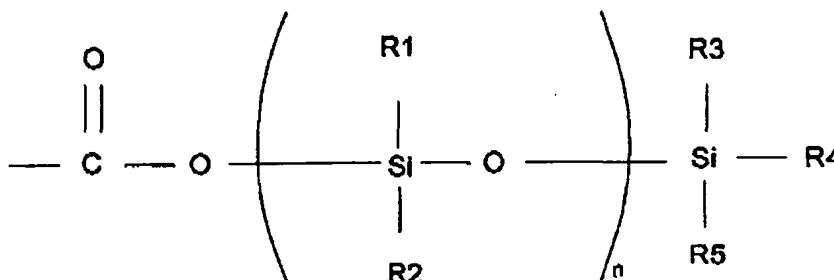
A water-reactive polymer can alternatively be a film-forming polymer comprising quaternary ammonium groups and/or quaternary phosphonium groups bound (pendant) to the backbone of the polymer. These quaternary ammonium groups  
25 and/or quaternary phosphonium groups are neutralised or, in other words, blocked or capped by counter-ions. Said counter-ions consist of the anionic residue of an acid having an aliphatic, aromatic, or alkaryl hydrocarbon group comprising at least 6 carbon atoms. Such systems are for instance described in PCT/EP03/007693.

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A further example of a suitable water-reactive polymer is a silyl ester copolymer comprising at least one side chain bearing at least one terminal group of the formula (I):



- 5 wherein  $n$  is 0 or an integer of 1 to 50, and R1, R2, R3, R4, and R5 are each independently selected from the group consisting of optionally substituted  $\text{C}_{1-20}$ -alkyl, optionally substituted  $\text{C}_{1-20}$ -alkoxy, optionally substituted aryl, and optionally substituted aryloxy.

10 Preferably, at least one of the groups R1-R5 in the silyl ester copolymer is methyl, isopropyl, *n*-butyl, isobutyl, or phenyl. More preferably,  $n$  is 0 and R3, R4, and R5 are the same or different and represent isopropyl, *n*-butyl, or isobutyl.

15 A silyl ester copolymer comprising at least one side chain bearing at least one terminal group of the above-described formula (I) can, for example, be obtained by copolymerising one or more vinyl polymerisable monomers with one or more monomers comprising one or more olefinic double bonds and one or more of the above-described terminal groups (I).

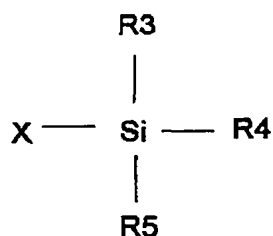
20 Examples of suitable vinyl polymerisable monomers, which can be copolymerised with one or more monomers comprising one or more olefinic double bonds and one or more of the above-described terminal groups (I), include (meth)acrylate esters such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, 2-hydroxyethyl methacrylate, and methoxyethyl methacrylate; maleic acid esters such as dimethyl maleate and

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diethyl maleate; fumaric acid esters such as dimethyl fumarate and diethyl fumarate; styrene, vinyl toluene,  $\alpha$ -methyl-styrene, vinyl chloride, vinyl acetate, butadiene, acrylamide, acrylonitrile, (meth)acrylic acid, acrylic acid, isobornyl methacrylate, maleic acid, and mixtures thereof. Preferably, a mixture of methyl  
 5 (meth)acrylate or ethyl (meth)acrylate with another vinyl polymerisable monomer is used. It is possible to adjust the polishing rate of the coating by using a mixture of a hydrophobic and a hydrophilic (meth)acrylate. Optionally a hydrophilic comonomer is included such as methoxy ethyl (meth)acrylate or a higher polyethylene oxide derivative, such as ethoxy ethyl (meth)acrylate,  
 10 propoxy ethyl (meth)acrylate, butoxy ethyl (meth)acrylate, a polyoxyethylene glycol monoalkyl ether (meth)acrylate, such as polyoxyethylene (n=8) glycol monomethyl ether methacrylate, or N-vinyl pyrrolidone.

Examples of suitable monomers comprising one or more olefinic double bonds and one or more of the above-described terminal groups (I), which can be  
 15 copolymerised with one or more vinyl polymerisable monomers, include monomers comprising one or more of the terminal groups (I) in which  $n = 0$ , and which may be represented by the formula (II):



wherein R3, R4, and R5 are as defined above, and X is a (meth)acryloyloxy  
 20 group, a maleinoyloxy group, or a fumaroyloxy group.

The preparation of the monomers (II) can, for example, be performed according to the methods described in EP 0 297 505, or according to the methods described in EP 1 273 589 and the references cited therein. Examples of suitable (meth)acrylic acid-derived monomers include: trimethylsilyl  
 25 (meth)acrylate, triethylsilyl (meth)acrylate, tri-n-propylsilyl (meth)acrylate,

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trisisopropylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate, triisobutylsilyl (meth)acrylate, tri-tert-butylsilyl (meth)acrylate, tri-n-amylsilyl (meth)acrylate, tri-n-hexylsilyl (meth)acrylate, tri-n-octylsilyl (meth)acrylate, tri-n-dodecylsilyl (meth)acrylate, triphenylsilyl (meth)acrylate, tri-p-methylphenylsilyl (meth)acrylate, tribenzylsilyl (meth)acrylate, dimethylphenylsilyl (meth)acrylate, dimethylcyclohexyl (meth)acrylate, ethyldimethylsilyl (meth)acrylate, n-butyl-  
5 dimethylsilyl (meth)acrylate, t-butyl-  
dimethylsilyl (meth)acrylate, diisopropyl-n-butylsilyl (meth)acrylate, n-octyldi-n-butylsilyl (meth)acrylate, diisopropylstearylsilyl (meth)acrylate, dicyclohexylphenylsilyl (meth)acrylate, t-butyl-  
10 diphenylsilyl (meth)acrylate, and lauryldiphenylsilyl (meth)acrylate. Preferably, trisisopropylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate, or triisobutylsilyl (meth)acrylate is used in the preparation of the silyl ester copolymer.

15 Alternatively, such a water-reactive acid-functional film-forming polymer the acid groups of which are blocked may be a carboxylic acid-functional polymer. For example, it may be a copolymer of acrylic or methacrylic acid with one or more alkyl acrylates or methacrylates, at least some of the acid groups of which have been converted to groups of the formula -COO-M-OH, wherein M is a  
20 divalent metal such as copper, zinc, calcium, magnesium or iron, as described in GB 2,311,070.

Another example of such a water-reactive acid-functional film-forming polymer the acid groups of which are blocked is a polymer that is a salt of an amine. Preferably it is a salt of an amine containing at least one aliphatic hydrocarbon  
25 group having 8 to 25 carbon atoms and an acid-functional film-forming polymer as described in EP 0 529 693, the acid-functional polymer preferably being an addition copolymer of an olefinically unsaturated carboxylic acid, sulphonic acid, acid sulphate ester, phosphonic acid or acid phosphate ester and at least one olefinically unsaturated co-monomer, the unsaturated carboxylic acid for  
30 example being acrylic or methacrylic acid, the unsaturated sulphonic acid for

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example being 2-acrylamido-2-methylpropane sulphonic acid (AMPS), and the film-forming polymer preferably being an amine sulphonate copolymer containing units of an organocyclic ester as described in WO 99/37723.

- 5 As an example of a suitable polymer (B) that is slightly soluble or water-sensitive in water the following compounds can be mentioned: polyvinyl methyl ether, polyvinyl ethyl ether, alkyd resins, modified alkyd resins, polyurethanes, saturated polyester resins, and poly-N-vinyl pyrrolidones.
- 10 As an example of a suitable polymer (B) that is insoluble in water, the following compounds can be mentioned: modified alkyd resins, epoxy polymers, epoxy esters, epoxy urethanes, polyurethanes, linseed oil, castor oil, soy been oil, and derivatives of such oils.

Other examples of suitable water-insoluble polymers or resins are: vinyl ether  
15 polymer, for example a poly(vinyl alkyl ether), such as polyvinyl isobutyl ether, or a copolymer of a vinyl alkyl ether with vinyl acetate or vinyl chloride, an acrylate ester polymer such as a homopolymer or copolymer of one or more alkyl acrylates or methacrylates which preferably contain 1 to 6 carbon atoms in the alkyl group and may contain a co-monomer such as acrylonitrile or styrene,  
20 and a vinyl acetate polymer such as polyvinyl acetate or a vinyl acetate vinyl chloride copolymer.

Alternatively, the water-insoluble polymer or resins can be a polyamine, particularly a polyamide having a plasticising effect such as a polyamide of a fatty acid dimer or the polyamide sold under the Trademark "Santiciser".

25

If in addition to the film-forming polymer (A), the coating composition comprises another resin or a mixture of other resins, these other resin(s) can form up to 80 percent by weight of the total amount of resins in the coating composition.

Preferably, the other resin forms up to 20 percent of the total resins in the  
30 coating composition to obtain a self-polishing coating of high quality.

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The polymers forming the film-forming binder can be mixed in a common solvent which forms at least part of the paint solvent, for example an aromatic hydrocarbon such as xylene, toluene or trimethylbenzene, an alcohol such as  
5 n-butanol, an ether alcohol such as butoxyethanol or methoxypropanol, an ester such as butyl acetate or isoamyl acetate, an ether-ester such as ethoxyethyl acetate or methoxypropyl acetate, a ketone such as methyl isobutyl ketone or methyl isoamyl ketone, an aliphatic hydrocarbon such as white spirit, or a mixture of two or more of these solvents. The paint can alternatively be  
10 water-based.

The antifouling coating composition according to the present invention additionally may comprise sparingly soluble pigments having a solubility in water of 0.5 to 10 parts per million which are not biocides for aquatic  
15 organisms. Examples of such pigments include zinc oxide, barium sulphate, calcium sulphate, and dolomite. Mixtures of sparingly soluble biocidal or non-biocidal pigments can be used, for example cuprous oxide, cuprous thiocyanate or copper pyrithione which are highly effective biocidal pigments, can be mixed, optionally with a non-biocidal soluble pigment such as zinc oxide.

20

In addition to copper-based biocides for aquatic organisms having a low metallic copper content, the antifouling coating composition can contain one or more non-metalliferous biocides for aquatic organisms, i.e. an ingredient having aquatic biocidal properties that is a biocide, but not a pigment. Examples of  
25 such compounds are tetramethyl thiuram disulphide, methylene bis(thiocyanate), captan, pyridinium triphenylboron, a substituted isothiazolone such as 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, 2-methylthio-4-t.butylamino-6-cyclopropylamino-s-triazine, N-3,4-dichlorophenyl-N',N'-dimethyl-urea ("Diuron"), 2-(thio-cyanomethylthio)benzothiazole, 2,4,5,6-tetrachloro-  
30 isophthalonitrile, dichlorofluanid, tolylfluanid, 2-(p-chlorophenyl)-3-cyano-4-



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bromo-5-trifluoromethyl pyrrole, 3-butyl-5-(dibromomethylidene)-2(5H)-furanone  
3-(benzo(b)thien-2-yl)-5,6-dihydro-1,4,2-oxathiazine-4-oxide, L-menthol, 5-  
methyl-2-(isopropyl)-cyclohexanol and 2,3,5,6-tetrachloro-4-(methyl-  
sulphonyl)pyridine. Optionally, the antifouling composition comprises one or  
5 more acid-functional biocides, for example, (9E)-4-(6,10-dimethylocta-9,11-  
dienyl) furan-2-carboxylic acid and p-(sulpho-oxy) cinnamic acid (zosteric acid).

Many of these non-metalliferous biocides are solid and all sparingly water-  
soluble and may help the "self-polishing" action of the paint.

10

The coating composition can additionally contain a pigment which is not  
reactive with water and may be highly water-insoluble (solubility below 0.5 part  
per million by weight) such as titanium dioxide or ferric oxide or an organic  
pigment such as a phthalocyanine or azo pigment. Such highly insoluble  
15 pigments are preferably used at less than 60% by weight of the total pigment  
component of the paint, most preferably less than 40%. The coating  
composition can additionally contain conventional thickeners, particularly  
thixotropes such as silica, bentonite or polyamide wax and/or stabilisers, for  
example zeolites or aliphatic or aromatic amines such as dehydroabietylamine.

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The paints used in the present invention are substantially free of rosin material  
and substantially free of any biocidal zinc moiety. For the present application  
this means that the paint comprises less than 5 wt.% of rosin and less than 5%  
of biocidal zinc moieties. Preferably, the paint comprises less than 1 wt.% of  
25 rosin and less than 1 wt.% of biocidal zinc moieties, more preferred the paint  
comprises less than 0,1 wt.% of rosin and less than 0,1 wt.% of biocidal zinc  
moieties, the wt.% being calculated based upon the total content of the paint.

The paint that is substantially free of any biocidal zinc moieties and  
30 substantially free of rosin is normally applied as a topcoat. As such it can be

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applied in the normal coating scheme for new build vessel. However, it is also possible to use it as a topcoat in the maintenance and repair of existing vessel and it can also be applied as a topcoat over a coating layer that contains biocidal zinc and/or a rosin material.

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Within the framework of the present application, an ocean water aquatic environment is an aquatic environment which has a salinity of approximately 35 practical salinity units (psu, a unit which is based on conductivity measurements), a high salinity aquatic environment is an aquatic environment which has a salinity of between about 15 and 35 psu, a low salinity aquatic environment is an aquatic environment which has a salinity of less than about 15 psu, and a fresh water aquatic environment is an aquatic environment which contains less than about 1000 mg/litre total dissolved solids. Examples of low salinity aquatic environments are river estuaries and semi-enclosed marine environments with high fresh water inputs and restricted exchange with ocean water, such as the Baltic Sea. Examples of fresh water aquatic environments are rivers, lakes and other surface waters.

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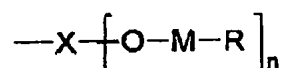
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**Claims**

1. Antifouling coating composition that is substantially free of any biocidal zinc moieties and substantially free of rosin, comprising a copper-based biocide  
5 for aquatic organisms having a metallic copper content below 2 % by weight, based on the total weight of the copper-based biocide, and a film-forming resin comprising

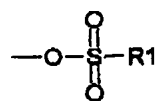
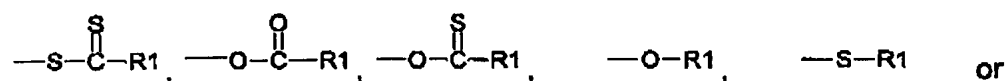
- 20-100% by weight of a film-forming polymer (A) having an acrylic backbone bearing at least one terminal group of the formula:



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wherein X represents  $-\overset{\text{O}}{\parallel}{C}-$ ,  $-\overset{\text{S}}{\parallel}{C}-$ ,  $-\overset{\text{O}}{\parallel}{P}-$  or  $-\overset{\text{O}}{\parallel}{P}-$

M is a copper or tellurium; n is an integer of 1 to 2; R represents an organic residue selected from



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; and R1 is a monovalent organic residue, and

- 80-0% by weight of a non-hydrolyzing water-insoluble film-forming polymer (B).

2. Antifouling coating composition according to claim 1, characterized in that  
20 the film-forming polymer (A) is an acrylic polymer in which X represents



3. Antifouling coating composition according to claim 1, characterized in that the copper-based biocide for aquatic organisms is cuprous oxide having a

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metallic copper content below 2 % by weight, based on the total weight of the cuprous oxide.

4. Antifouling coating composition according to claim 3, characterized in that the cuprous oxide has a metallic copper content below 1% by weight, based on the total weight of the cuprous oxide.

5. Antifouling coating composition according to claim 1, characterized in that the composition comprises copper pyrithione as copper based biocide.

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6. Antifouling coating composition according to claim 3, characterized in that the film-forming polymer (A) is an acrylic polymer in which X represents  $\text{—}\overset{\text{O}}{\parallel}\text{C—}$ , M is copper and R represents  $\text{—O—}\overset{\text{O}}{\parallel}\text{C—R1}$  and wherein the composition also comprises copper pyrithione as copper based biocide.

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7. A process for protecting a man-made structure immersed in a low salinity aquatic environment wherein an antifouling coating composition according to claim 1 is used.
8. Man-made structure immersed in low salinity aquatic environment coated with a coating composition according to claim 1.

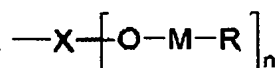
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**Abstract**

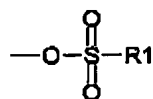
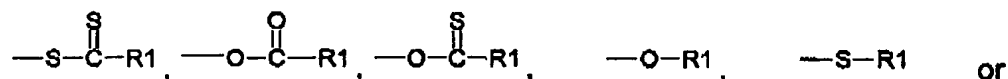
Antifouling coating composition that is substantially free of any biocidal zinc moieties and substantially free of rosin, comprising a copper-based biocide for aquatic organisms having a metallic copper content below 2 % by weight, based on the total weight of the copper-based biocide, and a film-forming resin comprising

- 20-100% by weight of a film-forming polymer (A) having an acrylic backbone bearing at least one terminal group of the formula:



wherein X represents  $-\overset{\text{O}}{\parallel}{C}-$ ,  $-\overset{\text{S}}{\parallel}{C}-$ ,  $-\overset{\text{O}}{\parallel}{P}-$  or  $-\overset{\text{O}}{\parallel}{P}<$

M is a copper or tellurium; n is an integer of 1 to 2; R represents an organic residue selected from



; and R1 is a monovalent organic residue, and

- 80-0% by weight of a non-hydrolyzing water-insoluble film-forming polymer (B).